The use of artificial intelligence methods in studying quantum intramolecular vibrational dynamics

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Artificial intelligence methods are used to treat the time evolution in intramolecular quantum dynamics. Comparison is made of several AI search algorithms and evaluation functions in an application to the study of quantum intramolecular vibrational redistribution. A combination of a beam search and a best-first search is used, in conjunction with an accumulated evaluation function which encourages both searching and ultimately satisfying the uncertainty principle. The methods developed are applied to an 11-coordinate heavy central mass problem and used to treat both quantum beats and "dissipative" intramolecular energy transfer. Good agreement is obtained with the "exact" quantum dynamics.

I. INTRODUCTION

The quantum mechanical study of intramolecular vibrational redistribution (IVR) in complex molecules is often limited by the computational time associated with the use of a large number of states in high-dimensional systems. However, although a large number of vibrational states exist in the molecular system, only a small subset of these states might be involved in any particular excitation and in the ensuing dynamics. Examples of such selective couplings have been found experimentally, for example, in the study of vibrational quantum beats[1] and in high resolution Doppler-free spectroscopy.[2] This subset is limited both by energetics and by couplings. The development of efficient and convenient methods which can identify the subset of important zeroth-order states should provide one approach to the practical solution of IVR problems.

In many IVR problems, a description of the redistribution of probability from an initial vibrational excitation is desired. This process can be viewed as the probability starting in an initial state and largely flowing through some subset of states in the molecule. In this paper, AI techniques[3,4] are used to find the most important subset of states from the many possible zeroth-order states. The states in the zeroth-order description can be ordered to form paths as illustrated later in Fig. 1 and discussed in detail later. If any single state in a relevant path is excluded, the description of the dynamics can be dramatically changed. Thus, since entire paths are desired, AI searching techniques, which generally find the most important paths first, are ideally suited as an aid in the solution of such quantum dynamics problems. Once the important subset of states is found by an AI method, the dynamics can be analyzed using this reduced block of states of the full Hamiltonian. The specific search methods are designed to obtain this subset of states and reproduce with them the important features of the dynamics of the full Hamiltonian.

Several papers have appeared in which AI techniques have been used to solve various problems, for example, in multiphoton dynamics,[5] vibrational eigenvalues,[6] computational physics,[7] and organic syntheses.[8] These papers have shown the feasibility of a variety of AI methods in their respective applications. The strength of AI search methods lies in their ability to search efficiently many possible zeroth-order paths which could be important to the process. In the present case, the paths are found while utilizing the selection rules of the Hamiltonian which limit the possible nonzero coupled states, and an evaluation function is implemented which gives an estimate of the importance of each state in actual dynamics. A preliminary account of some of the present methods has been given elsewhere.[9]

In Sec. II several search algorithms and their applicability to the IVR problem are discussed, while in Sec. III a number of possible evaluation functions are examined for estimating the importance of possible zeroth-order states. An 11-coordinate IVR model with a heavy central mass is described in Sec. IV and used in Sec. V for comparing the different search algorithms and evaluation functions. The results of the different AI methods are discussed in Sec. VI, followed by some conclusions in Sec. VII.

II. SEARCH ALGORITHMS

The use of AI search methods combines the use of search algorithms and evaluation functions. The search algorithm determines the order in which possible zeroth-order paths are considered. The evaluation function provides an estimate of the importance of the possible zeroth-order paths in the dynamics. The search algorithm will generally use the estimates of the evaluation function in deciding what path or paths to consider. The search algorithms are discussed in the present section and the evaluation functions in the next section.

There are a number of different types of search algorithms which have been proposed in the AI field and their efficiency and accuracy depends upon the type of problem to which they are applied.[3] In AI searching, the possible direct paths from an initial state (or states) are considered. Subsequent states arising in the possible paths are then considered, and in the process a *directed graph* or *tree* is formed in which the states are connected by *directed arcs*. A path from an initial state can be found by following the directed arcs to a

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given destination state. One way to find the optimal path between these two states is to form the complete tree and consider all possible paths to definitely decide the best possible path. However, since the tree can be extremely large, or even infinite, such a method is generally intractable for large (many-state) problems. The alternative is to intelligently construct only part of the tree, i.e., the *search tree* or *subtree*, which includes the most important paths for a given problem. The challenge in the AI search field is determining search techniques which can reliably and efficiently yield the important subtree.

In the IVR problem the probability from the initial state will become distributed over a few or many final zeroth-order states, the *goal states*. In the present paper we focus on two types of search algorithms which seem best suited to our problem in IVR.[10] Both methods are combinations of beam and best-first searches.[3] A *beam search* considers all possible paths from *every* newly found state whose evaluation function is above a minimum value.[11] A *best-first* search considers the most promising of all incomplete paths first. Although a complete beam search can exhaust all possibilities, it can require inordinate amounts of computer time to find the best paths, especially when many couplings exist, as in our model. (The rapid escalation of states that need to be considered is the commonly referred to *combinatorial explosion*.) Instead, we use a compromise wherein a beam search is performed for the first two levels of searching and a best-first search is utilized thereafter. We found that using only a best-first search led to more restrictive initial choices and yielded less accurate results. Two search methods are used in the present article, each implemented utilizing the selection rules of the Hamiltonian to allow the algorithm to generate and explore only those states that have nonzero couplings from the state of interest. In AI terminology, the Hamiltonian can be used to form a special operator, the *successor operator*, which when applied to a chosen state yields all states that can be directly reached in a single step from the chosen state. The process of applying the successor operator to the state chosen for consideration next has been termed *expanding* the state and the expanded state is then termed a *parent*.

We use two specific algorithms, i.e., two search methods, for finding acceptable states. In the first search algorithm, which will be referred to as the *best complete paths search*, only states are accepted which form a complete path to one of a specified set of goal states. A *goal state* in this search method will be defined as one whose energy is within a given energy range of the initial state and whose evaluation function is above a certain minimum value. The intuitive reason for this type of search is that the prepared state (the initial state) has a certain spread in energy which is time-invariant. The zeroth-order basis states which will have large probability at long times will typically be close in energy to the initial state. This feature can be seen from the relationship of time and energy given by the uncertainty principle. In our calculations with this best complete paths search, a state will be chosen as a goal state if its energy difference from the initial state is less than twice the root mean square of the energy width σ of the wave function. Paths can include states that are outside the energy spread of the wave function, but these states are expected only to have significant probability for short times. Such states that are important at early times are frequently referred to in the literature on radiationless transitions and IVR as doorway states. In the present best complete paths search, final incomplete paths are not accepted, even if they have a higher evaluation function than a complete path. A minimum value was chosen for the evaluation function for a goal state such that the accepted paths had a reasonable contribution to the actual dynamics and, through experience, such that the excluded paths did not noticeably change the dynamics. With increasing deviation of the zeroth-order basis from the actual eigenstates of the system, the zeroth-order states that are farther away in energy from the initial state have a greater likelihood of having a significant probability at long times. This behavior could lead to important states being difficult to find by the best complete paths search algorithm.

In a second search algorithm, which we shall term the *best incomplete paths search*, there is no insistence that acceptable states lead to any one of a specific set of goal states. In the searching a beam search is again used for the first two levels in the search, and this search is followed by a best-first search for all subsequent steps. However, a goal state is now defined as the state which has the best evaluation function at *each* step of the best-first part of the search. These goal states are, in fact, the same as the states that are expanded at each step of the best-first search. All states in the path to any such goal state at each step are also accepted.

In each of our search algorithms we start from a given zeroth-order initial state and apply the successor operator to determine all states that are coupled to it. A value of the evaluation function is then assigned to each of these coupled states, states which we will designate as S_1. The successor operator is applied to all states in S_1 whose evaluation function is above a minimum value, one at a time. The newly formed states form a set S_2 and the evaluation function associated with each path to states in S_2 is assigned. A minimum value of the evaluation function was set for a state to be expanded further in the beam search (in general a different minimum from that chosen for the goal states). The minimum was chosen through experience, such that the states eliminated from consideration have essentially no effect upon the dynamics. A balance is sought between including too many states in the beam search and eliminating states from consideration which may be important to the dynamcis. At this point a beam search of the first two levels of the tree has been performed and the search continues as a best-first search. The states in the set S_2 are sorted by their evaluation function. If duplicate states, i.e., states which have been found by two different paths, are present in S_2, the state with lower evaluation function is removed from the latter. The state in S_2 with the highest (best) evaluation function is removed from S_2 and selected for consideration next. (The state is also placed in a separate parents' set of states P so that it is not considered again for expansion.[12]) The successor operator is applied to that state to form a set of states, S_3. The combined set of states of the new S_2 and S_3 are sorted by evaluation function and duplicates are removed as before.

The successor operator is applied to the state with the best evaluation function in $S_2 + S_3$ to form a set of states S_4, and the state chosen to expand is removed from $S_2 + S_3$ and placed in the set of parents P. All states in the new $S_2 + S_3$ and in S_4 are sorted with duplicates removed. The process is repeated (i.e., the successor operator is applied to the state with the best evaluation function in the new $S_2 + S_3 + S_4$, etc.) until a desired number of states are chosen. These search algorithms are not limited in any way by the length of the path but use the evaluation function to determine the best possible paths to pursue.

An example of the two search algorithms is given now and illustrated in Fig. 1. For both methods in this example the same states are considered in the search. In actual applications, the evaluation function and states considered can differ in the two search methods. The states are numbered in the order in which they are found, the first number above a line in Fig. 1 representing the number of each state and the next number giving the evaluation function for that state. Both searches begin with the initial state 1, and upon expansion by applying the successor operator the two states 2, 3 (S_1) coupled to 1 are found which have, say, an evaluation function of 1.5 and 1.0, respectively. The successor operator is applied to state 2 and then to state 3, since they both have an evaluation function above the assumed minimum value of, say 0.5, in the beam search. This procedure yields states 4, 5, 6 (S_2). The beam search for the first two levels is now complete and the search continues as a best-first search. Of the states that have not yet been expanded [4, 5, 6 (S_2)], the path to state 4 is seen to have the best evaluation function (Fig. 1) and state 4 is expanded to yield state 7 (S_3). State 4 is placed in the set of parent states (P). Let us suppose that state 7 is a duplicate of state 2. Since state 7 reached by the above path has a lower evaluation function than state 2, state 7 is removed from the list of states to consider. (This removal is represented by the "X".) Of the remaining states not yet expanded [5, 6 ($S_2 + S_3$)], state 5 has the highest evaluation function and is added to P. Application of the successor operator to state 5 yields states 8, 9 (S_4). This procedure applies to both search methods used. We stop the search here for brevity of presentation and illustrate the process of accepting the states next.

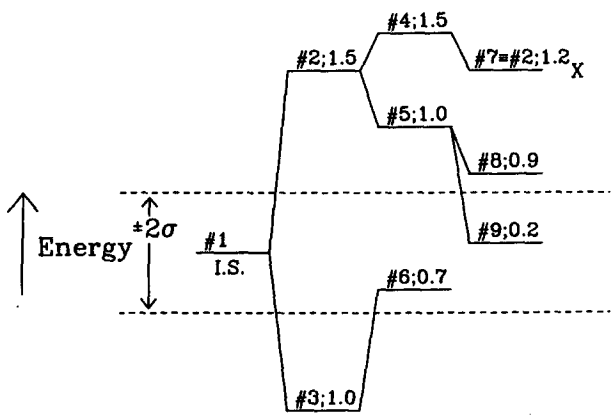

FIG. 1. Sample search tree for the two proposed search algorithms. The first number above each line is the number of the state and the second number the value of its evaluations function. The initial state (1,I.S.) has no evaluation function value associated with it. See the text for discussion of search.

The best complete paths search only accepts paths that lead to states that are within $\pm 2\sigma$ of the mean energy of the initial state (represented by the dotted lines in Fig. 1) and having at least the minimum value of the evaluation function. States 6, 9 are the only two states found by the above search which are within $\pm 2\sigma$ of the initial state. If the minimum acceptable evaluation function to be a goal state is 0.3, only state 6 is a goal state. Since the path leading to state 6 is included, states 1, 3, 6 are accepted.

In the best incomplete paths search, the path is accepted which leads to the state in the set of states which have not yet been expanded during the best-first search process and which has the highest evaluation function. Thus, state 4 with the path of states 1, 2 to state 4 is accepted first, since state 4 has the highest evaluation function of states 4, 5, 6. State 5 is accepted next, since it has the best evaluation function of states 5, 6 which are left after state 4 is expanded and duplicates removed. Since the path of states 1, 2 to state 5 is already accepted with a higher evaluation function, the states 1, 2 are not included again. Finally, state 8 is accepted since it has the best evaluation function of states 6, 8, 9. Thus, the best incomplete paths search accepts states 1, 2, 4, 5, 8, whereas the best complete paths search accepts states 1, 3, 6.

III. EVALUATION FUNCTIONS

Any chosen evaluation function should be simple enough that it can be quickly calculated, in order to provide an easy evaluation of the many possible choices of paths. The three evaluation functions below were motivated by perturbative expressions. (A discussion of the perturbative expressions is given at the end of this section.) They combine heuristically terms for both the energy difference from the initial state and the energy difference from the previous state. If the initial state in a path is numbered 1 and the final state in that path is numbered $n + 1$ there are $n - 1$ intermediate states and n links between the initial and final state. Three possible evaluation functions of this type are considered in this paper:

$$EF_1 = \left| V_{12} \prod_{i=2}^{n} \frac{V_{i,i+1}}{\frac{1}{2}(\Delta E_{i,i+1} + \Delta E_{1,i+1})} \right|,$$

$$EF_2 = \left| V_{12} \prod_{i=2}^{n} \frac{V_{i,i+1}}{\sqrt{(\Delta E_{i,i+1} \Delta E_{1,i+1})}} \right|,$$

$$EF_3 = \left| V_{12} \frac{1}{\Delta E_{1,n+1}} \prod_{i=2}^{n} \frac{V_{i,i+1}}{\Delta E_{i,i+1}} \right|, \tag{1}$$

where each factor after the product sign is set equal to unity whenever its magnitude exceeds unity, in analogy to an approximately degenerate perturbation theory for amplitudes. $V_{i,i+1}$ represents the matrix element between the i and $i + 1$ zeroth-order states and $\Delta E_{i,i+1}$ is the analogous energy difference. $\Delta E_{1,i+1}$ is the energy difference between the initial

state and state $i+1$. The terms after the product sign are only included for n greater than one. Also, all three evaluation functions can be defined recursively such that the evaluation function for the path with n links can easily be calculated using the value for the path with the first $n-1$ of these links.

Evaluation functions EF_1 and EF_2 give an equal weighting to the two energy differences $\Delta E_{i,i+1}$ and $\Delta E_{1,i+1}$, whereas evaluation function EF_3 includes the energy difference $\Delta E_{1,n+1}$ between the initial state and the *last* state in the path. This feature leads to the property that evaluation functions EF_1 and EF_2 are monotonically decreasing functions of n whereas EF_3 is not, since the energy difference from the initial state $\Delta E_{1,n+1}$ is only taken to the last state, $n+1$, in the path, and that state will change with increasing n. This nonmonotonic property leads to greater difficulties in using evaluation function EF_3, because its use is more likely to find paths with an evaluation function higher than that of some path previously chosen in the search. Because EF_3 generally caused a large reordering of the importance of paths by their evaluation function from level 1 to level 2, the minimum value for the evaluation function EF_3 in the beam search was set equal to zero, but not so for the other evaluation functions. When the best complete paths search is performed using EF_3, the $1/\Delta E_{1,n+1}$ term is deleted in computing the final evaluation function of the *final state*, a goal state. This deletion is made since no energy preference is given here to one state over another within the spread of the wave function. We also note that the deletion yields a final evaluation function in units of energy, the same units as EF_1 and EF_2.

From nth order perturbation theory, one of the matrix elements between state 1 and state n in a path is[13]

$$EF_4 = |V^n_{\text{eff}}| = \left| V_{12} \prod_{i=2}^{n} \frac{V_{i,i+1}}{\Delta E_{1,i+1}} \right| , \tag{2}$$

when $V_{i,i+1}/\Delta E_{1,i+1}$ is small. (In the actual perturbation expression many other terms are typically present.[13]) One choice of the evaluation function would be to use Eq. (2), but with each $V_{i,i+1}/\Delta E_{1,i+1}$ set equal to unity whenever this factor exceeds unity, so as to simulate very roughly the calculation of a local amplitude in a nearly-degenerate perturbation theory.

An alternative matrix element would be to consider each step in the path as involved in an independent step-by-step perturbation and only include the energy difference between the i and $i+1$ states:

$$EF_5 = |V^n_{\text{eff}}| = \left| V_{12} \prod_{i=2}^{n} \frac{V_{i,i+1}}{\Delta E_{i,i+1}} \right| , \tag{3}$$

with each $V_{i,i+1}/\Delta E_{i,i+1}$ being replaced by unity whenever it exceeds unity. The problem encountered in using EF_5 as the evaluation function is that the states found with optimal evaluation function have no preference to be near the energy of the initial state. In tests of EF_5, we sometimes found that the states with the largest couplings to the initial state are remote in energy from the initial state. Since all subsequent steps in the path have some energy difference from the previous state in the denominator, the states with the best evaluation function would stay near the energy of a state selected during the first step, if Eq. (3) were used for the evaluation function. This result would lead to the best incomplete paths search wandering off to energies far from the initial state and to the best complete paths search never or only rarely finding complete paths which return near the energy of the initial state in a reasonable amount of computer time.

Evaluation functions EF_1, EF_2, and EF_3 represent three choices which combine heuristically the energy difference to the initial state ($\Delta E_{1,i+1}$) and, to encourage the searching of possibly dynamically important states, the energy difference to the previous state ($\Delta E_{i,i+1}$). These choices combine the advantages of the two perturbation ideas in Eqs. (2) and (3).

Once the important subset of states is determined by the AI method, the dynamics can be performed with the reduced Hamiltonian formed from these states. For example, in the present paper the eigenvalues and eigenvectors were determined by matrix diagonalization from which the properties of physical interest were determined.

IV. MODEL SYSTEM

The AI methods were tested for an 11-coordinate IVR problem involving a heavy central mass.[14] The model represents the system C_a–C_b–M–CD_2–C_c, where M is a relatively heavy central mass that can act as a barrier to energy redistribution in the molecule and where C and D denote carbon and deuterium atoms.[15] C_a,C_b, and C_c have as effective masses those of CH_3, CH_2, and CD_3, respectively. The Hamiltonian for the system is given by

$$H = H_L + H_R + V_{LR} , \tag{4}$$

where

$$H_L = \frac{1}{2} \sum_{i=1}^{2} \sum_{j=1}^{2} G_{ij} P_i P_j + \sum_{i=1}^{2} D_i (1 - \exp[\alpha_i (r_i - r_i^e)])^2 , \tag{5}$$

$$H_R = \frac{1}{2} \sum_{i=3}^{11} \sum_{j=3}^{11} \left[\left(G'_{ij} + \sum_{k=3}^{11} \frac{\partial G'_{ij}}{\partial r_k} r_k \right) P_i P_j \right] + \frac{1}{2} \sum_{i=3}^{11} k_i (r_i - r_i^e)^2 , \tag{6}$$

$$V_{LR} = \lambda \frac{\cos\theta}{m} P_2 P_3 . \tag{7}$$

Here, r_i and P_i are the bond-coordinate and momentum, respectively. G_{ij} is the Wilson G matrix[16(a)] where its derivatives in Eq. (6) are evaluated at the equilibrium value of the bond-coordinates. The detailed parameters of this model are discussed elsewhere.[15] In the present tests H_L, the Hamiltonian for the left ligand of the molecule, contained two Morse

potentials for a nonbending chain, and that for the right ligand H_R contained only harmonic potentials. In addition, the kinetic energy coupling in H_R included a first order correction to the equilibrium G matrix term, thereby adding a nonquadratic term.[17] In the calculations, H_R was transformed using normal mode coordinates, obtained from diagonalizing the quadratic part of H_R.[16(a)] The bond modes consisted of two stretching coordinates in H_L, four in H_R, and five independent bending coordinates[16(b)] in H_R.

The Hamiltonian is written as having left (L) and right (R) contributions, so as to represent the physical notion of approximate separability of the motion of two ligands attached to a relatively heavy central atom. The basis set used in the calculations has as wave functions the product of a wave function of H_L and one of the normal modes of H_R, the latter found when the derivatives of the G matrix in H_R are omitted. H_L had been "prediagonalized" to yield wave functions of the left ligand, because of the high energies of excitation used for the left ligand. The λ parameter in V_{LR} allows for the variation of the kinetic coupling between left and right ligands in a way which mimicked changing the central mass M. The advantage of using λ instead of actually changing the central mass is that the frequencies of the left and right ligands remained unchanged. Thus, a "pure" mass effect is achieved in this model calculation without the possibility of resonances accidentally being modified.

The system was initially "prepared" in a zeroth-order state that only had excess energy in the left ligand (the initial wave function being a product of a prediagonalized state of H_L and the normal mode ground state of H_R). The quantum dynamics of the system were then determined by *full* matrix diagonalization of the zeroth-order basis set determined by the AI methods. A quantity of physical interest is the amount of energy in the left ligand of the molecule as a function of time, so as to determine the amount of IVR occurring between the ligands.

V. RESULTS

The two AI search algorithms and the five evaluation functions were compared with the best "exact" result, a result that was achievable in a reasonable amount of computer time by imposing a simple energy constraint on the zeroth-order states used in the calculation. In order to compare the AI methods to the exact result, the search was constrained to searching the same set of basis states used in the exact calculation. These calculations were performed so as to compare the quality of the different AI methods, with the ultimate goal of using the developed techniques without such a constraint on the basis states chosen, both for this and for other systems. In the present comparison, m in Eq. (7) has the mass of carbon and λ there is set equal to 0.5, 0.1012, and 0.1655, to represent the masses of twice carbon, tin, and germanium, respectively. In the exact calculations, the lighter mass system showed a greater dissipation of energy from the left ligand into the right, whereas the heavier mass system displayed instead vibrational quantum beats. Even though the latter resembled largely an effective two-state problem in an eigenstate representation in one example and an effective three-state problem in the other, it involved many zeroth-order basis states. These two modes of behavior, dissipation and quantum beats, represent different dynamical situations and serve to test the robustness of the present AI methods.

In Fig. 2 a plot of the time-dependence of the energy in the left ligand is given for the best incomplete paths search for the two evaluation functions that were best for that type of search (EF_1 and EF_4) for $\lambda = 0.5$. A comparison with the exact results is given where all zeroth-order basis states within $\pm$ 650 cm^{-1} of the initial state were used to give 1112 basis states. Although the agreement with exact results using both evaluation functions is good, the short-time agreement with the exact results is much better for EF_1 than for EF_4 (Fig. 2). Figure 3 is similar to Fig. 2, except that now $\lambda = 0.1012$. In this case, one of quantum beats, both EF_1 and EF_4 evaluation functions show good agreement with the exact results.

In Fig. 4 are shown results of the exact search, the best complete paths search with the evaluation function EF_3 that was best for this type of search, and the best incomplete paths search with EF_1, for $\lambda = 0.5$. In Fig. 5 the same methods are illustrated except that now $\lambda = 0.1012$. For both of these cases, the two AI search methods show good agreement with the exact result. In Fig. 6 results for a second, more complex quantum beats example is given using the same AI search algorithms and evaluation functions as in Fig. 5. Here, λ is 0.1655 and, since the energy of excitation is lower, the exact results now have 1023 basis states for all zeroth-order states within $\pm$ 1300 cm^{-1} of the initial state. For both AI methods 125 basis states were selected and in both cases good agreement was obtained with the exact results for the amplitude of the oscillations. However, overall, the best incomplete paths search with EF_1 gave better agreement with the exact result than did the best complete paths search with EF_3, the latter having a larger phase shift with respect to the exact result. This phase shift persisted even

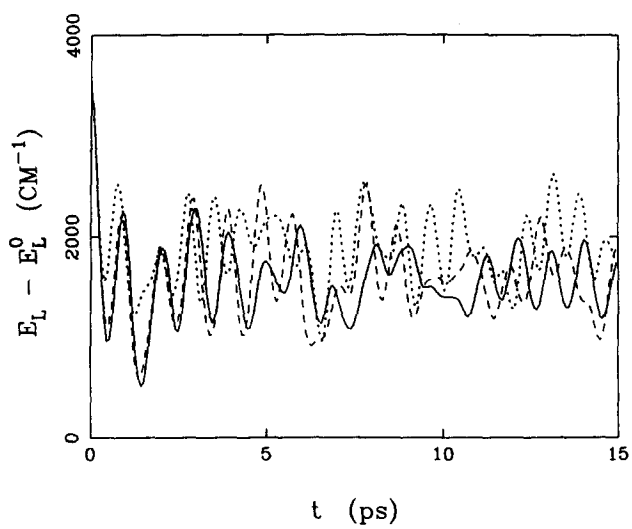

FIG. 2. Comparison of "exact" and the best incomplete paths search for the two best evaluation functions EF_1 and EF_4 best for that search. Energy in the left ligand is plotted vs time, for $\lambda = 0.5$ (2C) for the conditions given in Tables I(A) and I(B). The solid line (—) is the exact result, the dashed line (---) is for EF_1, and the dotted line (· · · ·) is for EF_4.

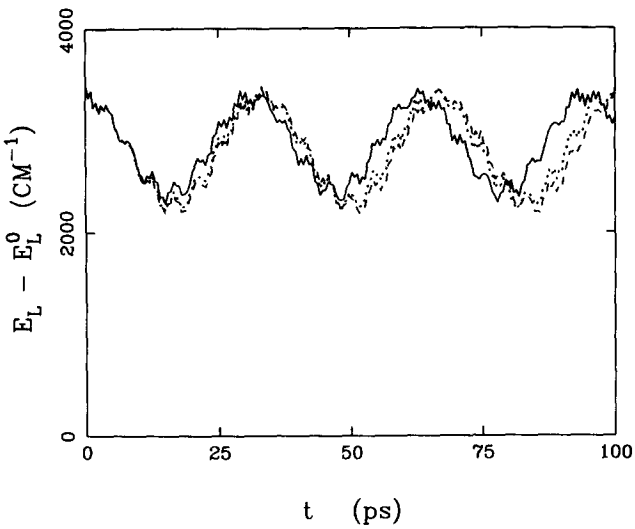

FIG. 3. Comparison of exact and the best incomplete paths search for the two evaluation functions EF_1 and EF_4. Energy in the left ligand is plotted vs time, for $\lambda = 0.1012$ (Sn) for the conditions given in Tables I(A) and I(B). Symbols are the same as in Fig. 2.

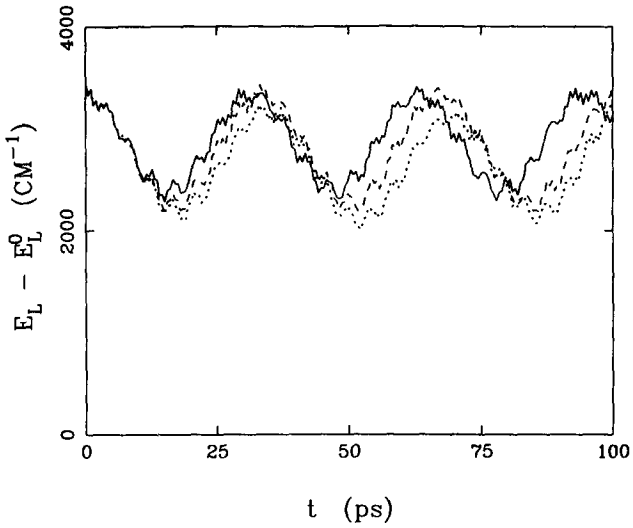

FIG. 5. Comparison of exact and the two preferred AI methods for energy in the left ligand vs time, for $\lambda = 0.1012$(Sn) for the conditions given in Tables I(A) and I(B). Symbols are the same as in Fig. 4.

when the basis set was increased to 175 states and is an example where the best complete paths search with EF_3 does not necessarily converge quickly toward the exact result.

In Tables I(A) and I(B) the different combinations of all the AI search algorithms and evaluation functions used are shown for the same excitation given in Figs. 2–5. For each of these calculations, the AI methods were used to find the same number of basis states for the same initial condition, so that a direct comparison could be made. The number of states chosen was the number required to give an approximate convergence by the two better procedures [as in Tables II(A) and II(B) given later]. Two quantitative measures were used to compare the different procedures: the long-time average of the energy in the left ligand $\langle E_L \rangle$, and the spread of energies in the left ligand σ_{E_L}, given by

$$\langle E_L \rangle = \lim_{T\to\infty} \frac{1}{T}\int_0^T E_L(t)dt,$$

$$\langle E_L^2 \rangle = \lim_{T\to\infty} \frac{1}{T}\int_0^T E_L^2(t)dt,$$

$$\sigma_{E_L} = [\langle E_L^2 \rangle - \langle E_L \rangle^2]^{1/2}. \tag{8}$$

Two additional quantitative measures were used for the tin system. They are the time period τ_{FT} corresponding to the dominant peak in the Fourier transform of $E_L(t)$ and its corresponding Fourier coefficient $\bar{A}_{FT}$, defined by

$$\bar{A}_{FT} = \int_{-\infty}^{\infty} E_L(t)\exp(i\omega t)dt, \tag{9}$$

with $E_L(-t) = E_L(t)$, and restricted to $\omega > 0$. $E_L(t)$ was

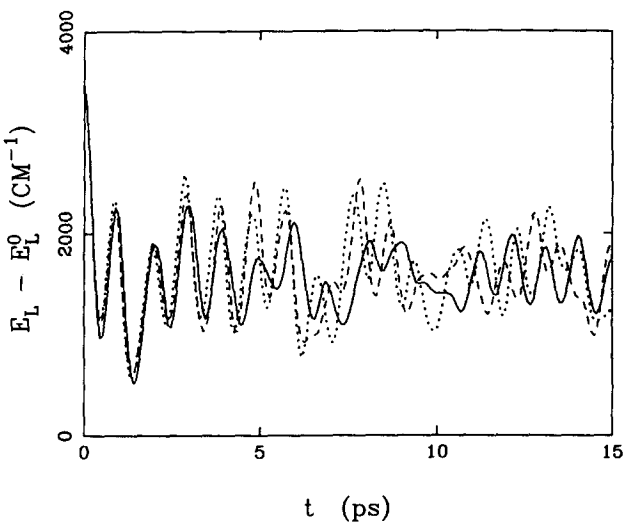

FIG. 4. Comparison of exact and the preferred AI methods for the energy in the left ligand vs the time, for $\lambda = 0.5$ (2C) for the conditions given in Tables I(A) and I(B). The solid line (—) is the exact result, the dashed line (- - -) is for best incomplete paths /EF_1, and the dotted line (· · · ·) is for best complete paths /EF_4.

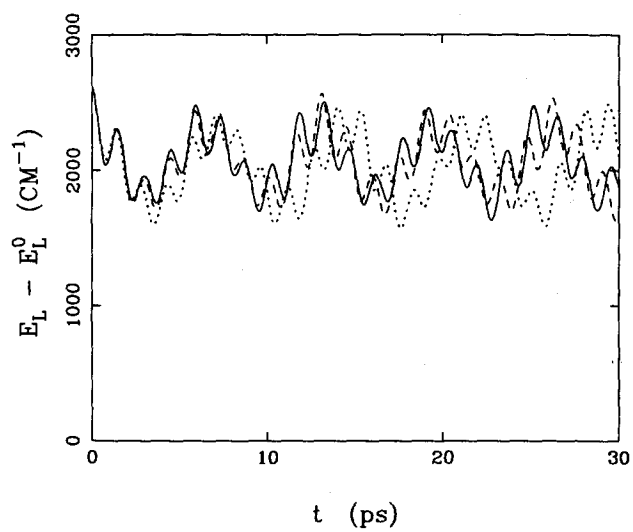

FIG. 6. Comparison of exact and the two preferred AI methods for energy in the left ligand vs time, for $\lambda = 0.1655$ (Ge) for an initial energy of excitation in the left ligand of 3500 cm^{-1}. Symbols are the same as in Fig. 4.

TABLE I. Comparison of AI evaluation functions for best incomplete and complete paths search.[a]

	$\lambda = 0.1012$, 70 states[b]				$\lambda = 0.5$, 20 states[b]	
Evaluation	$\lvert\%\Delta\langle E_L\rangle\rvert$[c]	$\lvert\%\Delta\sigma_{E_L}\rvert$[d]	$\lvert\%\Delta\tau_{FT}\rvert$	$\lvert\Delta A_{FT}\rvert$[d]	$\lvert\%\Delta\langle E_L\rangle\rvert$	$\lvert\%\Delta\sigma_{E_L}\rvert$
			(A) Incomplete			
EF_1	1.7	14	6.6	14	2.3	14
EF_2	5.9	47	18	49	3.6	15
EF_3	4.4	35	34	35	3.1	14
EF_4	1.2	10	4.9	10	14	15
EF_5	1.4	11	20	10	0.86	35
EF_1[e]	5.8	47	17	48	11	18
			(B) Complete			
EF_3[f]	4.7	13	9.4	11	3.7	15
EF_1	7.8	56	18	58	16	3.2
EF_2	7.1	54	20	56	16	3.2
EF_4	7.7	57	19	59	30	7.2
EF_5	5.1	41	19	42	17	12

[a] Values for "exact" results for $\lambda = 0.1012$ are $\langle E_L\rangle = 3834\ \text{cm}^{-1}$, $\sigma_{E_L} = 337\ \text{cm}^{-1}$, $\tau_{FT} = 32$ ps and $A_{FT} = 234\ \text{cm}^{-1}$. For $\lambda = 0.5$ the values are $\langle E_L\rangle = 2521\ \text{cm}^{-1}$ and $\sigma_{E_L} = 316\ \text{cm}^{-1}$. The initial energy in the left ligand is $4433\ \text{cm}^{-1}$, which includes a zero-point energy in the left ligand of $972\ \text{cm}^{-1}$. The minimum value for the evaluation function in the beam search (except EF_3) was generally $1\times10^{-3}\ \text{cm}^{-1}$. This value compares with the smallest evaluation function for an accepted path which was generally found to be $1\times10^{-2}\ \text{cm}^{-1}$ for $\lambda = 0.1012$ and $5.0\ \text{cm}^{-1}$ for $\lambda = 0.5$.

[b] The total number of states sometimes varied by a few, more or less, since only complete paths were included.

[c] Defined as $100(\langle E_L\rangle - \langle E_L^{\text{exact}}\rangle)/\langle E_L^{\text{exact}}\rangle$, and similarly for the other quantities.

[d] It is readily shown from Eqs. (8) and (9) that for a pure cosine curve $\sigma_{E_L} = \sqrt{2}A_{FT}$.

[e] A pure best-first search is used, as discussed in text.

[f] The minimum value of the evaluation function for a goal state for EF_3 was $7.5\times10^{-3}\ \text{cm}^{-1}$ for $\lambda = 0.1012$ and $10\ \text{cm}^{-1}$ for $\lambda = 0.5$. The minimum values for the other evaluation functions varied, depending on the range of values found for the evaluation function.

expressed in terms of the wave functions of the system and gave rise, upon integration of Eq. (9), to one or more delta-like functions of ω at the differences of eigenvalues resulting from the diagonalization. The period and amplitude A_{FT} are reported at these delta functions. The dominant peak in the Fourier transform characterizes the dominant oscillation that acts as an *effective* two-state oscillation and, in the case of the results in Table I(B), had a coefficient that was approximately one order of magnitude larger than that of the next most important peak. All values in Tables I(A) and I(B) are given as the absolute value of the percent difference from the exact result.

Although none of the methods are totally unacceptable, the best incomplete paths search with evaluation function EF_1 appears to be the first choice, and the best complete paths search with evaluation function EF_3 the second choice. These results are given at the top of Tables I(A) and I(B). Of these two procedures the former gave better results for the conditions in Fig. 6. These two procedures are seen to be the best at reproducing *both* types of dynamical situations, as illustrated in the visual comparison in Figs. 2–5. In the final row of Table I(A) results are given using the evaluation function EF_1 when a pure best-first search was performed for *all* levels of searching.[18] As we remarked earlier, these results using EF_1 in a pure best-first search are less accurate than using EF_1 in the combined beam search and best-first search in the present best incomplete paths search. In Tables II(A) and II(B), the convergence of the two best AI methods are shown as a function of the number of basis functions chosen. The results show that the two procedures tend to approach the exact result as the number of basis states is increased, as judged with the quantitative measures employed in Tables I(A) and I(B). Figure 6, however, shows an example where the best complete paths search with EF_3 is very slow to converge to the exact result.

An additional example is given in Table III using these two best AI procedures for the model Hamiltonian, for the case that the search for basis states was not constrained by energy, i.e., where the condition $\Delta E \leqslant 650\ \text{cm}^{-1}$ was not imposed. No exact calculations are given now, since it was not presently computationally practical to include the many thousands of zeroth-order states that are within the range of energies included by the present AI results when the dynamics is performed by full matrix diagonalization. The parameter λ was varied from 1 to 9.9 to mimic the masses of Sn, Ge, Ti, Si, and C [where the central mass m in Eq. (7) is now that of Sn]. The AI procedure was used to select a subset of 1000 states while considering over one million possible states. (For a problem studied with 1.5 million states, examining samples of up to 200 000 states, and extrapolating, about 15% of the 1.5 million states were estimated not to be duplicates.) In Table III the long-time average energy in the left ligand is given. The agreement of the results obtained with the two different procedures is very good, with the largest difference being for carbon, where the zeroth-order basis set is least like the eigenstates.

TABLE II. Comparison of convergence of the two preferred AI methods as a function of number of basis states chosen for $\lambda = 0.1012$ and $\lambda = 0.5$.[a]

(A) $\lambda = 0.1012$

	Best incomplete paths $/EF_1$[b]				Best complete paths $/EF_3$[b]			
# Basis	$\%\Delta\langle E_L\rangle$[c]	$\%\Delta\sigma_{E_L}$	$\%\Delta\tau_{FT}$	$\%\Delta A_{FT}$	$\%\Delta\langle E_L\rangle$	$\%\Delta\sigma_{E_L}$	$\%\Delta\tau_{FT}$	$\%\Delta A_{FT}$
30	1.9	−13	−30	−13	4.0	−30	−38	−30
50	−7.6	61	22	63	4.7	−36	−34	−36
70	−1.7	14	6.6	14	4.7	13	9.4	11
90	−3.6	1.1	4.6	−1.2	−4.4	18	10	17

(B) $\lambda = 0.5$

	Best incomplete paths $/EF_1$[b]		Best complete paths $/EF_3$[b]	
# Basis	$\%\Delta\langle E_L\rangle$[c]	$\%\Delta\sigma_{E_L}$	$\%\Delta\langle E_L\rangle$	$\%\Delta\sigma_{E_L}$
10	17	20	14	5.7
20	2.3	14	3.7	15
30	−4.3	6.2	−2.7	12
40	−1.4	3.8	−0.29	11

[a] Footnote a of Table I.
[b] Footnote b of Table I.
[c] Footnote c of Table I.

VI. DISCUSSION

The results show that both the type of search algorithm and the evaluation function are important in IVR problems. As seen in Tables I(A) and I(B) the same evaluation function can give very different results when used with a different search algorithm. Further, the results show that inclusion of a weighting factor that employs both the energy difference from the initial state $\Delta E_{1,i+1}$ and from the previous state $\Delta E_{i,i+1}$ leads to a better overall AI evaluation function for the present problem than the use of either one alone.

Of all the methods presented, the two AI procedures that were best in reproducing *both* types of dynamical situations are listed, as already noted, at the top of Tables I(A) and I(B), with the best incomplete paths search with EF_3 having an edge (Fig. 6). Even though they give similar qualitative results, implementation of these two procedures is quite different. Evaluation function EF_3 can have both increases and decreases in the evaluation function, whereas EF_1 is monotonically decreasing. The variations in the value of EF_3 implies that a better path can be found at a later time in the search process from a path that had in an earlier stage a lower evaluation function. This situation leads to additional complications in verifying the convergence of the AI method when EF_3 is used. Furthermore, the best complete paths search needs additional parameters not present in the best incomplete paths search. One such parameter is the minimum acceptable evaluation function for a *final* path and the other is the assigned energy range for acceptable final states to form paths. It is also shown in Tables II(A) and II(B) that the best incomplete paths search converges, for the examples studied, more rapidly for most measures of accuracy than the best complete paths search. Additionally, it is seen in Tables I(A) and I(B) that the best incomplete paths search has a lesser dependence on the specific details of the evaluation function used than the best complete paths search. In summary, the best incomplete paths search was easier to implement and with it the AI searches were performed more quickly.

One nice feature of the use of an AI method is in identifying the states that are important to the dynamics. Originally, before we considered applying an AI method to IVR, we had found some of the important states in an energy transfer path by considering the overlap (squared) of the wave function with each of the basis states as a function of time. By examining these overlaps as a function of time at very short times, six successive important states in a path were found for the $\lambda = 0.1012$ case. The states had greater than one percent overlap at all short-time points examined. However, with both AI methods not only were these six states found first in the search, but then states were found with less than one percent overlap at short times but important to the dynamics. Without these latter states, the period of oscillation and the amplitude of the fluctuations of the energy in the left ligand as a function of time had an error of approximately 40%. Thus, with these two AI methods states with highest overlap were found first and then states were found that had small overlap but were dynamically important.

It should be stressed that the AI search is performed

TABLE III. Comparison of $\langle E_L\rangle$ for the two preferred AI methods on a model Hamiltonian with 1000 AI-selected basis states.[a]

Mass	Best incomplete paths $/EF_1$ $\langle E_L\rangle$	Best complete paths $/EF_3$ $\langle E_L\rangle$
Sn	4120	4094
Ge	3627	3718[b]
Ti	3465	3289
Si	2831	2736
C	2829	3226

[a] The initial energy in the left ligand is 4582 cm^{-1} which includes a zero-point energy in the left ligand of 727 cm^{-1}.
[b] AI method was only able to find 717 states in a reasonable amount of computer time (less than 3 h on a VAX 11/780).

within the set of zeroth-order states. Thus, the AI method is not a replacement for an intelligent choice of the model or the zeroth-order description. (Indeed, the A in AI might better denote "automated" rather than "artificial"!) The larger discrepancies between the results of the AI procedures in Table III for carbon than for the other central atoms may be due to the much larger left/right couplings of the zeroth-order basis, due to the increased breakdown of the separation of variables for the two ligands in the case of the central atom having a mass comparable to the other masses.

One final aspect is the amount of computer time required by the AI method to find the states of importance. Though our codes are not optimized for speed the best incomplete paths search took 10 to 20 min on a VAX 11/780 for the results given in Table III. (The best complete paths search took 40 min to 3 h.) Once the AI search was complete, the time to perform the dynamics on the 1000 states selected by the AI method was then 150 s on a Cray X-MP, a time which may be loosely equated to 30 h of VAX 11/780 time. Typically, in fact, the time spent doing the AI searches was a small percent of the total computer time needed to solve the problem.

VII. CONCLUSIONS

The development of AI search methods is seen to represent a significant step forward in the abilty to study IVR problems with many degrees of freedom. The AI technique is a method for identifying the important dynamical states from thousands or millions of zeroth-order states. The determination of the dynamics from a Hamiltonian with millions of states is beyond the scope of presently available methods.[19] Furthermore, the computer time necessary for performing the AI methods on higher energy excitations of a molecule is comparable to that of lower molecular energies states, provided the number of possible states searched by the AI method is the same. This is especially encouraging since the total number of available states increases exponentially with energy.

In the present paper we have systematically compared several possible choices for search algorithms and evaluation functions. These comparisons, which were made for two common dynamical situations in IVR, quantum beats, and dissipation, should prove helpful in application of AI methods to a variety of IVR problems. The AI methods presented in this paper are implemented in a modular fashion, such that all of the search and decisions sections of the code can easily be used in various IVR problems. Only the sections of the code that involve the description of the Hamiltonian and the specific evaluation function desired need to be changed for each specific application. Thus, the present AI methods are not only promising but can be easily applied to a range of potential applications.

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[10] Due to the removal of duplicate states in our search algorithm, it is possible to overlook secondary paths to the same state. Consideration of duplicate states adds complexity to the algorithm and slows the search process. We tested several cases with our model where duplicate paths were allowed. In most cases the results were less accurate and required two to four times longer for the search to be performed. In the best case, the improvement over the method where duplicate states were excluded was only 2.2%. Although the duplicate states are not important in our model calculations, they might (with their additional paths) be important in other dynamcial situations. We found, however, that the states in the secondary paths to the same state tended to be included through important paths to other states when duplicates were excluded. Furthermore, the two search algorithms proposed tend to omit different paths leading to duplicates. They form thereby a consistency check for these possibilities.

[11] A beam search reduces to a breadth-first search if the minimum value of the evaluation function is zero.

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